Chinese Science Bulletin

March 2012 Vol.57 No.7: 832
doi: 10.1007/s11434-011-9953-z

$R_2Mn_2Se_2O$ (R = LaO and BaF): A new layered manganese oxyselenide with an antiferromagnetic checkerboard spin lattice

Transition metal oxides have a long and distinguished history. They exhibit many interesting and intriguing properties due to the correlated-electron effect. Recently, Professor Chen Xianhui and his group from Hefei National Laboratory for Physical Science at Microscale and Department of Physics, University of Science and Technology of China synthesized two new manganese oxychalcogenides, $R_2Mn_2Se_2O$ [R = (LaO) and (BaF)], which are isostructural to the previous Fe and Co analogs. Their work, entitled "Structural and magnetic properties of the layered manganese oxychalcogenides $(LaO)_2Mn_2Se_2O$ and $(BaF)_2Mn_2Se_2O$", was published in Volume 83 of *Physical Review B*.

The discovery of noncopper high-T_C iron-based pnictides with two-dimensional FeAs layers revived intense interest in the layered transition-metal oxychalcogenides or oxypnictides. The titanium oxypnictides RTi_2Pn_2O [R = Na_2, Ba, $(SrF)_2$, and $(SmO)_2$, Pn = As and Sb] have a spin-density-wave (SDW)/charge-density-wave (CDW) instability corresponding to an anomalous transition in resistivity, susceptibility, Hall coefficient, etc., similar to the properties of iron pnictides. The transition metal oxychalcogenides $R_2Fe_2Q_2O$ [R = (BaF), (SrF), and (LaO), Q = S and Se] are isostructural to the titanium oxypnictides. The previous studies found that the Fe analogs formed long-range AFM ordering below 83–106 K and were Mott insulators due to narrowing of the Fe d-electron bands and corresponding enhancement of correlation effects. More recently, $(LaO)_2Co_2Se_2O$, isostructural to $(LaO)_2Fe_2Se_2O$, was also synthesized. It was an insulator and had an AFM transition at T_N ~220 K. Based on density-functional calculations, the researchers suggested that the square-lattice Mott insulator $La_2O_2Co_2Se_2O$ had a more stable high-spin (S = 3/2) ground state with considerably strong magnetic frustration.

The other new layered manganese oxychalcogenides, $(LaO)_2Mn_2Se_2O$ and $(BaF)_2Mn_2Se_2O$, isostructural to $(LaO)_2Fe_2Se_2O$, were synthesized by solid-state reactions. The single crystals of the former compound were also successfully grown using fusion method. These layered compounds are composed of a stack of the fluorite type $[Ln_2O_2]$ or $[AE_2F_2]$ (Ln = rare earth elements; AE = alkali earth metal) alternating regularly with the rock-salt or antifluorite $[M_nQ_m]$ type. These compounds show some high two-dimensional physical properties. $(LaO)_2Mn_2Se_2O$ crystallizes in $I4/mmm$-symmetry and edge-shared $[Mn_{4/2}Se_2O_{4/4}]^{2-}$ layers interspersed by fluorite-type $[La_2O_2]^{2+}$ layers along the c-axis. In the $[Mn_{4/2}Se_2O_{4/4}]^{2-}$ unit, Mn is located between two O^{2-}, forming a square planarlayer of $Mn_{4/2}O$, and two Se^{2-} are located above and below the center of the $Mn_{4/2}O_{4/4}$ square unit, which is an anti-configuration to the $CuO_{4/2}$ layer observed in high-T_C cuprates. For such Se/O-mixed tetragonal structure, there are three intralayer spin-exchange interactions: AF exchange J1 via corner-sharing Mn-O-Mn, AF exchange J2 via face-sharing Mn-O-Mn/Mn-Se-Mn, and FM exchange $J3$ via edge-sharing Mn-Se-Mn. These spin-exchange interactions induce magnetic frustration in these compounds with checkerboard spin lattices.

The as-prepared $(LaO)_2Mn_2Se_2O$ and $(BaF)_2Mn_2Se_2O$ samples both show insulating behavior and have higher resistivity than those of $(LaO)_2Fe_2Se_2O$ and $(BaF)_2Fe_2Se_2O$. In addition, the resistivity obeys thermally activated behavior and can be fitted by the Arrhenius equation $\rho = \rho_0 \exp(E_a / k_B T)$, where ρ_0 is the pre-exponential factor and k_B is the Boltzmann constant. The obtained activation energy E_a is 278 and 416 meV for $(LaO)_2Mn_2Se_2O$ and $(BaF)_2Mn_2Se_2O$, respectively.

The dc magnetic susceptibility $\chi(T)$ of polycrystalline $(LaO)_2Mn_2Se_2O$ shows a broad maximum around 360 K, suggesting low-dimensional antiferromagnetism or two-dimensional short-range ordering due to strong magnetic frustration. Below 360 K, $\chi(T)$ decreases as temperature decreases to 50 K. In this decreasing $\chi(T)$, a small anomaly is observed at 161 K, which may suggest a magnetic transition at this temperature. A broad maximum is also observed in $\chi(T)$ for polycrystalline $(BaF)_2Mn_2Se_2O$ at a temperature of 210 K. Moreover, $\chi(T)$ for the single-crystal $(LaO)_2Mn_2Se_2O$ sample was also measured with the magnetic field applied in the ab plane or along the c axis. There is a distinct transition at T_N ~161 K in $\chi(T)$ for single crystals. In addition, the susceptibility of single crystal samples shows strong anisotropic magnetic properties below T_N, suggesting that the spins spontaneously align predominantly along the c axis. The heat capacity further confirms the magnetic transition. There is a very slight anomaly around 161 K for $(LaO)_2Mn_2Se_2O$ and 101 K for $(BaF)_2Mn_2Se_2O$ in specific heat measurement. Compared with Mn analogs, the Fe and Co analogs had a sharp peak in specific heat around T_N. This suggests more frustrated magnetic correlation in Mn analogs than in Fe or Co analogs above T_N.

The researchers suggest that while being analogs to the isostructural iron and cobalt oxychalcogenides, these newly synthesized Mn-based compounds may also be Mott insulators with an antiferromagnetic ground state. The susceptibilities of polycrystals and single crystals suggest short-range magnetic ordering or low-dimensional AFM ordering above T_N due to considerably strong magnetic frustration in these compounds. These intrinsic magnetic behaviors are helpful in understanding the underlying physics of these rare transition-metal oxychalcogenides or oxypnictides with a frustrated AFM checkerboard spin lattice.

This work was supported by the National Basic Research Program of China (2011CB00101), the National Natural Science Foundation of China (51021091), the Specialized Research Fund for the Doctoral Program of Higher Education of China (200803580040), and Chinese Academy of Sciences.

See the article: Liu R H, Zhang J S, Cheng P, et al. Structural and magnetic properties of the layered manganese oxychalcogenides $(LaO)_2Mn_2Se_2O$ and $(BaF)_2Mn_2Se_2O$. Phys Rev B, 2011, 83: 174450